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THE NEAR ULTRAVIOLET ABSORPTION SPECTRA OF ORTHO-, META-, AND PARA-FLUOROANILINES

M. A. SHASHIDHAR AND K. SURYANARAYANA RAO

DEPARTMENT OF PHYSICS, KARNATAK UNIVERSITY, DHARWAR-3

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Plate 1 & 2

ABSTRACT. The near ultraviolet absorption spectra of the vapours of the ortho-, meta-, and para-fluoroanilines were photographed and analysed. The spectrum of the ortho-fluoroaniline consists of about 25 red-degraded bands in the region 3065–2750A and with the band at 34584 cm^{-1} as (0,0), these bands can be interpreted in terms of ten ground state and eight upper state fundamentals. About 35 red-degraded bands are recorded in the spectrum of the meta-isomer in the region 2950–2685A and are explained on the basis of nine ground state and twelve upper state fundamentals with the band at 34620 cm^{-1} chosen as (0,0). In the spectrum of the para-molecule, about 25 red-degraded bands are observed in the region 3100–2710A and are interpreted in terms of two ground state and nine upper state frequencies, taking the band at 32669 cm^{-1} as the (0,0) band. The assignments of the fundamentals chosen in these molecules are correlated with the Raman data where available.

INTRODUCTION

Although the ultraviolet absorption spectra of aniline and of some substituted anilines were investigated, substituted anilines still require a systematic study. In view of this, a study of the near ultraviolet absorption spectra of fluorinated anilines, namely, ortho-, meta-, and para-fluoroanilines, was carried out. A preliminary note giving the results has already been published (Shashidhar and Suryanarayana Rao, 1965). In this paper are reported the details of the investigation. The Raman spectrum of para-compound has been studied by Kohlrausch and Ypsilanti (1935). The Raman spectra of the other two molecules, namely, ortho-, and meta-molecules do not seem to have been observed yet. There are, however, interpolated Raman spectra of these molecules (Kohlrausch and Vogel & Hertey 1947). There do not seem to be any infra-red spectral data available yet on these molecules.

EXPERIMENTAL

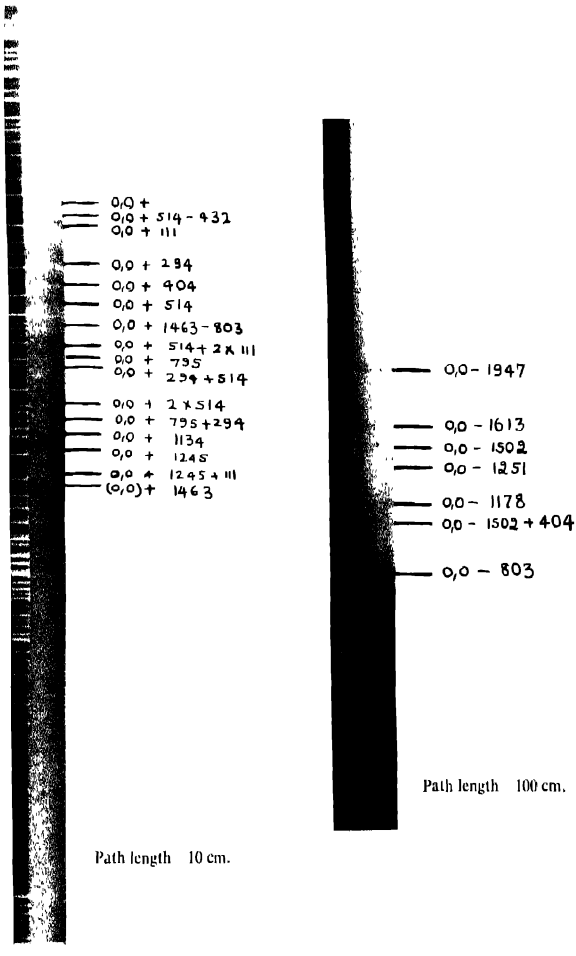
The samples of ortho-, meta-, and para-fluoroanilines used in this investigation were obtained from Light Co, England. The boiling points of ortho-, meta-, and para-fluoroanilines are 175°C, 186°C, and 187·6°C respectively. They

were purified by distilling three times in vacuum sealed tubes and this distilled product was used for further work. The absorption tube was an all quartz one of different lengths with fused plane quartz windows (lengths 5 cms, 10 cms, 25 cms and for higher path lengths quartz to pyrex graded seals were used). The absorption cell was evacuated continuously with intermittent heating so as to degas the tube. The distilled product was then introduced into the side limb of the absorption tube and then suddenly the temperature of the side limb was lowered by immersing it in a cooling mixture and the whole system was then evacuated for about half an hour and the tube was sealed off. Under these conditions, the substance in the absorption tube would be approximately at its saturated vapour pressure. For temperatures higher than the room temperature it was found desirable to keep the main body of the absorption tube at about 10° C higher in temperature than the container so as to eliminate the possibility of the vapour condensing on the inside and the windows of the tube. Hilger hydrogen lamp run on a stabilised direct current hydrogen lamp power supply unit FL16 was used as a source of continuum. Spectrograms were taken on Ilford R-40 and G-30 plates employing a Hilger medium quartz spectograph. Exposure times varied from 30 minutes to 7 hours. Absorption path lengths 5 cms, 10 cms, 25 cms, 50 cms, 75 cms, 100 cms were used. The temperature of the absorption cell was varied from −10°C to 150° C. Each band was measured on three different spectrograms using a Hilger comparator with reference to the standard iron arc lines and using Hartmann's dispersion formula, and the mean value of the different determinations was taken for the wavelength of each band. Band heads were measured in the case of sharp bands and centres in the case of diffuse bands. Intensities are visual estimates. The accuracy of measurements has been estimated to be about 5 cm^{-1} for the sharp bands and about 10 cm^{-1} for broad or diffuse bands.

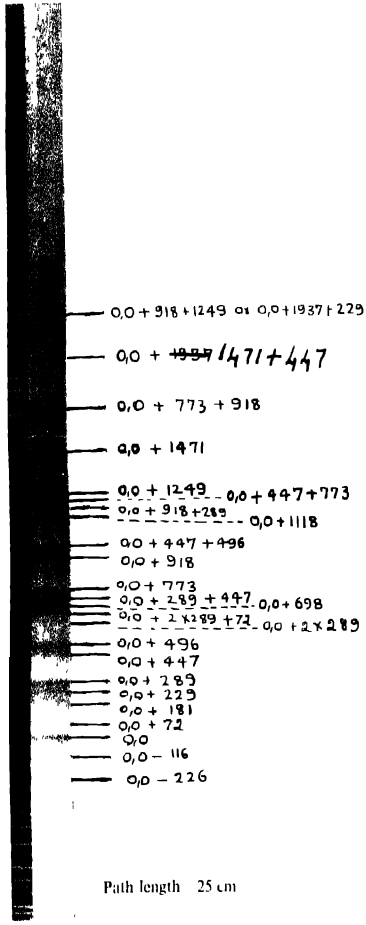
RESULTS

Ortho-fluoroaniline. The absorption spectrum of this molecule lies in the region 3065.4–2750 Å. The bands are rather sharp and degraded to the red. The spectra were photographed with path lengths 5 cm, 10 cm, 50 cm, 75 cm, and 100 cm at room temperature and at temperatures between −10°C to 150° C. The maximum number of bands are obtained with a 10 cm cell at room temperature. At higher temperatures the absorption on the violet side grows stronger and becomes continuous and more bands gradually appear on the red end of the continuum. The amount of vapour in the absorption cell was adjusted as described earlier. The longest wavelength sole band at 3063 Å is recorded at room temperature using at 100° cm cell.

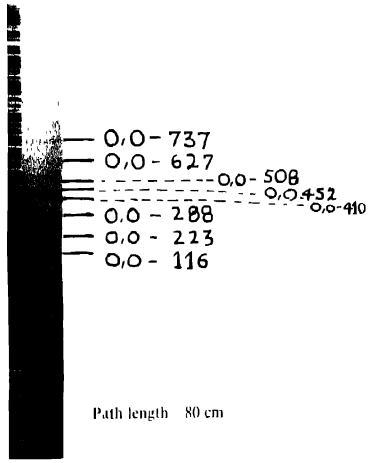
Meta-fluoroaniline. The absorption spectrum lies in the region 2950 Å to 2685 Å. The bands are sharp and degraded to the red. The maximum number



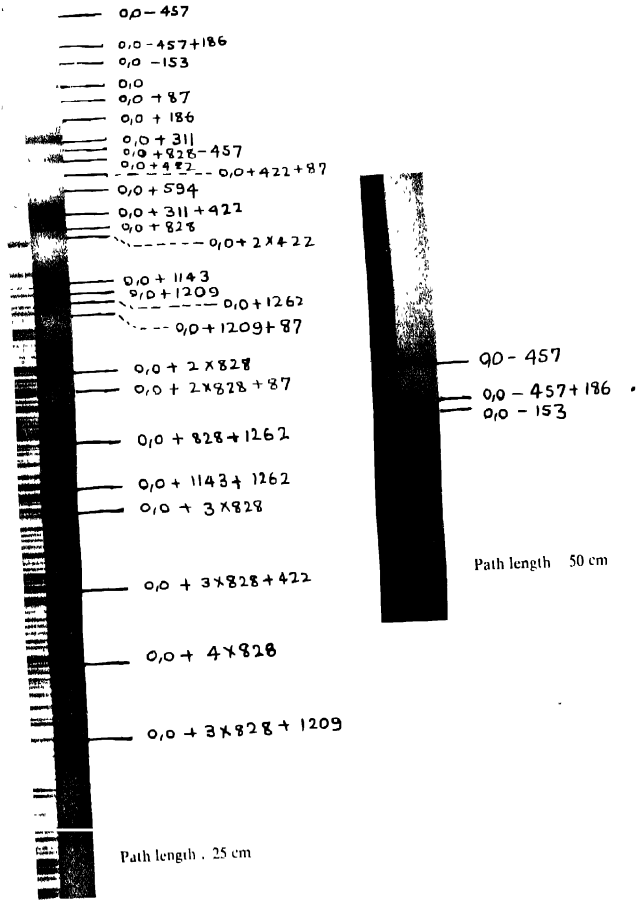
Ultraviolet absorption spectrum of ortho-fluoroaniline vapour at room temperature



Ultraviolet absorption spectrum of meta fluoroaniline vapour at room temperature.



Ultraviolet absorption spectrum of meta fluoroaniline vapour at room temperature



Ultraviolet absorption spectrum of Para fluoroaniline vapour at room temperature.

of bands are recorded with a 25 cm at room temperature. The effect of increasing temperature and path length is the same as in the case of ortho-compound.

Para-fluoroaniline. The bands of the para-isomer lie in the region 3100 Å to 2710 Å. Some of the bands are somewhat sharp and the others are rather broad and they are all degraded to the red. The effect of increasing temperature and path length is the same as in the case of ortho-and meta-fluoroanilines. The maximum number of bands are recorded with a 25 cm cell at room temperature.

The first two columns of each of tables I, II and III give the wave numbers in vacuum of the bands and their visually estimated intensities respectively of ortho-, meta-, and para-fluoroanilines.

ANALYSIS AND DISCUSSION

Ortho-fluoroaniline. This molecule belongs to the point group C_s. The molecule has only one element of symmetry namely, the plane of molecule assuming NH_2 to be a single unit and the whole molecule to be planar, which is a plane of symmetry. The transition, which is $A' - A'$, is an allowed one with the transition moment lying in the molecular plane.

The minimum number of bands for this isomer are recorded with a 5 cm cell at $-10°C$. Of these, the one lying at the longest wave length side at 34584 cm^{-1} is chosen as the (0, 0) band of the system. The strong bands on its long wavelength side with separations 261, 350, 432, 564, 803, 1178, 1251, 1502, 1613 and 1947 cm^{-1} are identified as the ground state fundamentals, while the strong bands on its short wavelength side with shifts 111, 294, 404, 514, 795, 1134, 1245, 1463 cm^{-1} are assigned as the fundamentals of upper electronic state of the system. These ten ground state and eight upper state fundamentals can account for almost all the bands of the system. The separations of the bands of the ortho-fluoroaniline from the (0, 0) band and their assignments are given in columns 3 and 4 respectively of table I.

Meta-fluoroaniline. Meta-fluoroaniline like the ortho-isomer, belongs to the point group C_s. The minimum number of bands for this isomer are recorded with a 5 cm cell at $-10°C$. Of these, the one lying on the long wavelength side at 34620 cm^{-1} is taken as the (0, 0) band of the system. The strong bands with separations 116, 223, 288, 410, 452, 508, 627, 737, 846 cm^{-1} from the (0, 0) band towards the longer wavelength side are assigned as the ground state fundamentals. The strong bands with shifts 72, 181, 229, 289, 447, 496, 698, 773, 918, 1118, 1249 and 1471 cm^{-1} from (0, 0) on its violet side are taken as the fundamentals of the upper state. On the basis of these nine ground state and twelve upper state fundamentals, all the bands of this isomer can be assigned. Columns 3 and 4 of table II respectively give the shifts of the bands from the (0, 0) band and their assignments.

TABLE I

Ultraviolet absorption bands of ortho-fluoroaniline

Wave number (vacuum) in cm^{-1}	Relative Intensity	Shift from 0,0 band in cm^{-1}	Assignment
32637	2	−1947	0,0−1947 (0,0−350−2×803)
32917	2	−1613	0,0−1613 (0,0−2×803)
33082	2	−1502	0,0−1502
33333	0	−1251	0,0−1251
33406	2	−1178	0,0−1178
33480	2	−1104	0,0−1502+404
33781	3	− 803	0,0−803
34020	1	− 564	0,0−564
34152	1	− 432	0,0−432
34234	1	− 350	0,0−350
34323	1	− 261	0,0−261
34584	5	0	0,0
34657	0	73	0,0+514−432
34695	4	111	0,0+111
34878	4	294	0,0+294
34988	4	404	0,0+404
35098	3b	514	0,0+514
35249	1b	665	0,0+1463−803
35338	0bd	754	0,0+514+2×111
35379	1	795	0,0+795
35406	1	822	0,0+294+514
35617	0b	1033	0,0+2×514
35653	0bd	1069	0,0+795+294
35718	0bd	1134	0,0+1134
35829	0b	1245	0,0+1245
35947	1b	1363	0,0+1245+111
36047	0b	1463	0,0+1463

b = broad;
bd = broad and diffuse.

TABLE II

Ultraviolet absorption bands of meta-fluoroaniline

Wave number (vacuum) in cm^{-1}	Relative Intensity	Shift from 0,0 band in cm^{-1}	Assignment
33774	0	— 846	0,0—846
33883	0	— 737	0,0—737
33993	1	— 627	0,0—627
34046	0	— 571	0,0—2 288
34112	3	— 508	0,0— 508
34168	1	— 452	0,0— 452
34210	5	— 410	0,0 -410
34332	2b	— 288	0,0—288
34397	4	— 223	0,0—223
34504	2	— 116	0,0—116
34620	7	0	0,0
34692	0	72	0,0 + 72
34801	2	181	0,0+181
34849	4	229	0,0+229
34909	5	289	0,0+289
35067	3	447	0,0+447
35116	4	496	0,0+496
35208	0d	588	0,0+2×289
35269	1d	649	0,0+2×289+72
35318	2	698	0,0+698
35360	1	740	0,0+289+447
35393	5	773	0,0+773
35474	0b	854	0,0+773+72
35538	2	918	0,0+918
35588	2	968	0,0+447+496
35738	2	1118	0,0+1118
35817	2	1197	0,0+918+289
35837	1	1217	0,0+447+773
35869	2	1249	0,0+1249

TABLE II—*contd.*

Wave number (vacuum) in cm^{-1}	Relative Intensity	Shift from 0,0 band in cm^{-1}	Assignment
36091	2b	1471	0,0+1471
36300	1b	1680	0,0+773+918
36464	0b	1844	0,0+2×918
36557	0b	1937	0,0+1471+447
36786	0b	2166	0,0+918+1249
36902	0b	2282	0,0+2×918+447 or 0,0+2×1249−223
37036	0b	2416	0,0+1471+447+496
37186	0bd	2566	0,0+2×1249+72
37249	0bd	2629	0,0+2×918+773

b = broad; bd = broad and diffuse.

TABLE III

Ultraviolet absorption bands of para-fluoroaniline

Wave number (vacuum) in cm^{-1}	Relative Intensity	Shift from 0,0 band in cm^{-1}	Assignment
32212	1	− 457	0,0−457
32407	1	− 262	0,0−457+186
32516	2	− 153	0,0−153
32669	7	0	0,0
32756	0	87	0,0+87
32855	0	186	0,0+186
32980	7	311	0,0+311
33025	0	356	0,0+828−457
33091	6	422	0,0+422
33193	0	524	0,0+422+87
33263	1	594	0,0+594
33418	7	749	0,0+311+422
33497	6	828	0,0+828
33523	1	854	0,0+2×422

TABLE III—*contd.*

Wave number (vacuum) in cm	Relative Intensity	Shift from 0 0 band in cm	Assignment
33812	3	1143	0,0 + 1143
33877	2	1209	0,0+1209
33931	2	1262	0,0+1262
33988	2	1319	0,0+1209+87
34325	2b	1656	0,0+2×828
34421	1	1752	0,0+2×828+87
34751	1b	2082	0,0+828+1262
35055	1b	2386	0,0+1143+1262
35168	2bd	2499	0,0+3×828
35548	1bd	2879	0,0+3×828+422
35995	0bd	3326	0,0+4×828
36362	0bd	3693	0,0+3×828+1209

b = broad, bd = broad and diffuse

Para-fluoroaniline This molecule belongs to the point group C_{2v}. The bands belong in this case, to the transition $A_1 \rightarrow B_1$ with the transition moment lying in the molecular plane and perpendicular to the para-axis.

The minimum number of bands for this molecule are recorded with a 5 cm cell at 10° C and of these, the one which lies on the longer wavelength side at 32669 cm^{-1} is chosen as (0, 0) band On the red side of the (0 0) band are two bands with shifts 153, 457 cm^{-1}. These may be assigned as ground state fundamentals and correlated with Raman frequencies 164 and 452 cm^{-1} The following strong bands on the violet side of the (0, 0) band at 87, 186 311, 422, 594, 828, 1143 1209, 1262 cm^{-1} are identified as the upper state fundamentals Almost all the observed bands can be explained in terms of these two ground state and nine upper state fundamentals. Column 3 of table III gives the shifts of the observed bands from the (0, 0) band while column 4 gives their assignments.

It may be mentioned that in this molecule despite the fact that the spectra were taken under different possible experimental conditions not more than three bands have been obtained on the red side of the (0, 0) band. Two of these bands have been assigned as ground state fundamentals In contrast, in the ortho-, and meta-, isomers, many ground state fundamentals have been obtained. We have no explanation for this rather strange feature in the para-molecule.

The assignments of most of the bands are indicated on reproductions in plates 1, 2 and 3. Since the preliminary note on this investigation, referred to earlier, was sent up for publication, the analyses have been slightly revised and with these slightly revised analyses, it has been possible to assign almost all bands

TABLE IV

Fundamental frequencies of ground and excited states of ortho-, meta-,para-fluoroanilines

Ground State frequencies in cm^{-1}						Excited State frequencies in cm^{-1}		
Ultraviolet absorption (present work)			Raman data			Ultraviolet absorption (present work)		
ortho-	meta-	para-	ortho- (Interpolated Raman Spectra)	meta-	para- (Observed)	ortho-	meta-	para-
—	116 (2)	153 (2)	—	—	164 (2)	111 (4)	72 (0)	87 (1)
—	223 (4)	—	195 (St)	220 (mst)	197 (0)	—	181 (0)	186 (1)
261 (1)	298 (2b)	—	285 (mst)	240 (mst)	—	—	229 (1)	—
350 (1)	410 (5)	—	330 (m)	350 (m)	362 (3)	294 (4)	289 (5)	311 (7)
564 (1)	508 (3)	—	535 (mst) 585 (SSt)	530 (St) 515 (m)	635 (1)	514 (3b)	496 (4)	594 (1)
432 (1)	452 (1)	457 (1)	448 (m)	—	452 (4)	404 (4)	447 (3)	422 (6)
—	627 (1)	—	—	605 (m)	—	—	—	—
—	737 (0)	—	765 (St)	740 (St)	—	—	698 (2)	—
803 (3)	846 (0)	—	860 (St)	— 950 (SS)	844 (4b)	795 (1)	773 (5)	828 (6)
—	—	—	1030 (SSt)	1000 (St)	—	—	918 (2)	—
1178 (2)	—	—	—	—	1150 (0)	1134 (0bd)	1118 (2)	1143 (3)
—	—	—	—	—	1218 (0)	—	—	1209 (2)
1251 (0)	—	—	1270 (St)	1298 (St)	1265 ($\frac{1}{2}$)	1245 (0b)	1249 (2)	1262 (2)
1502 (2)	—	—	—	—	—	1463 (0b)	1471 (2b)	—
1613 (2)	—	—	1580 (m) 1600 (m)	1590 (m)	1510 (0)	—	—	—
1947 (2)	—	—	—	—	—	—	—	—

in the spectra. It may be seen that the fundamentals, however, remain nearly the same.

Some alternative assignments for some of the bands in these spectra as overtones and combinations may be possible, as indeed we find they are. But we prefer the assignments given in the tables because we feel that the bands we have chosen as fundamentals are a little too intense to be regarded as combinations or or overtones This argument also applies to the band 1947 cm $^{-1}$ in the ortho-molecule. Further, along with the ultra-violet absorption work we have also recorded and analysed the infra-red spectra in the liquid state of these molecules (communicated) and the analyses of these infra-red spectra confirm our assignments of the fundamentals in the present work.

The correlations between the ground state fundamentals from Raman spectra and the present work and the upper state fundamentals obtained from the present work are indicated in table IV for the three molecules.

It may be mentioned that the agreement between the ground state fundamentals observed in ultra violet absorption in the present work and the interpolated Raman spectra in the case of ortho-, and meta-isomers is, in some cases, not satisfactory but it may not be too surprising, considering that the available Raman spectra of these molecules are not observed ones but only interpolated ones.

The shifts of the (0, 0) bands from that of benzene are 3506, 3469 and 4520 cm^{-1} in ortho-, meta-and para-molecules respectively. The shifts in the ortho-, and meta-somers are nearly equal whereas the para-molecules exhibits a markedly large shift This influence of the para-position fluorine atom on the shift of the (0, 0) band is also displayed by para-fluorotoluene, (Cave and Thompson, 1950) where the shift is 1212 cm^{-1} as compared to 691 cm^{-1} in meta-, and 513 cm^{-1} in ortho-isomers. This is observed also in para-difluorobenzene (Cooper, 1954), para-fluorobenzonitrile (Cooper, 1953), para-fluorochlorobenzene (Krishnamachari, 1957).

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REFERENCES

Cave and Thompson, 1950, *Faraday Soc. Discussions*, **9**, 35.
Cooper, C. D., 1953, *J. Chem. Phys.*, **21**, 379.
——— 1954, *J. Chem Phys.*, **22**, 503.
Kohlrausch, K. W. F. and Vogel.R & Herty.E. 1947, *Monatsh*, **76**, 200.
Kohlrausch, K. W. F. and Ypsilanti, 1935, *Monatsh*, **66**, 285.
Krishnamachari, S. L N. G., 1957, *Indian J. Phys.*, **31**, 447.
Shashidhar, M. A. and Suryanarayana Rao, K., 1965, *Current Science*, **34**, 479